

What is claimed is:

- 1    1. A composite electrolyte for use in electrochemical fuel cells, comprising:
  - 2       (i) an inorganic cation exchange material;
  - 3       (ii) a silica-based material; and
  - 4       (iii) a proton conducting polymer-based material, wherein the inorganic cation exchange material comprises about 0.1 wt% to about 99 wt% of the composite electrolyte.
- 1    2. The composite electrolyte of claim 1, wherein the silica-based material comprises about 0.1 wt% to about 70 wt%, and the proton conducting polymer-based material comprises about 0.1 wt% to 99.9 wt% of the composite electrolyte.
- 1    3. The composite electrolyte of claim 1 wherein the inorganic cation exchange material is selected from the group consisting of clay, zeolite, hydrous oxide, and inorganic salt.
- 1    4. The composite electrolyte of claim 3, wherein the clay includes an aluminosilicate-based exchange material selected from the group consisting of montmorillonite, kaolinite, vermiculite, smectite, hectorite, mica, bentonite, nontronite, beidellite, volkonskoite, saponite, magadite, kenyaita, zeolite, alumina, rutile.
- 1    5. The composite material of claim 3, wherein the clay is modified to make it more compatible with organic matrices, a clay modification including exfoliation which helps to separate platelets of inorganic substance.
- 1    6. The composite electrolyte of claim 3, wherein the clay includes a modified montmorillonite consisting of montmorillonite treated with a modifier material selected from a group consisting of aminododecanoic acid, trimethyl stearate ammonium, octadecylamine, and methyl dihydroxy hydrogenated tallow ammonium.
- 1    7. The composite electrolyte of claim 1 wherein the inorganic cation exchange material comprises about 0.1 wt% to about 30 wt%, the silica-based material comprises about 0.1 wt% to about 30 wt%, and the proton conducting polymer-based material comprises about 40 wt% to 99.9 wt% of the composite electrolyte.

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1       8.     The composite electrolyte of claim 1 wherein the proton conducting polymer-based  
2     material has a linear, branched, or network morphology.

1       9.     The composite electrolyte of claim 1 wherein the proton conducting polymer-based  
2     material includes material selected from the group consisting of  
3     acrylonitrile/butadiene/styrene rubber (ABS), styrene butadiene/acrylate/acetate polymer  
4     blends, epoxides, and a thermoplastic material.

1       10.    The composite electrolyte of claim 9 wherein the thermoplastic material is selected  
2     from a group consisting polypropylene, polycarbonate, polystyrene, polyethylene, polyaryl  
3     ethers sulfones, poly aryl ether ketone, and polysulfones.

1       11.    The composite electrolyte of claim 1 wherein the proton conducting polymer-based  
2     material has a functional group element selected from a group consisting of sulfonate,  
3     phosphate, carbonate, amide, and imide, wherein each such functional group element has  
4     proton conducting capabilities.

1       12.    The composite electrolyte of claim 1, further comprising an additive selected from a  
2     group consisting of preservative, thixotropy and viscosity control agent, crosslinking agent,  
3     conditioner, plasticizer, water control agent, and proton conducting material.

1       13.    The composite electrolyte of claim 1 wherein the inorganic cation exchange material,  
2     the silica-based material and the proton conducting polymer-based material comprise 90 wt  
3     % or more of the solids content of the composite electrolyte.

1       14.    The composite electrolyte of claim 1 wherein the composite electrolyte when  
2     measured in the substantially dried state consists essentially of the inorganic cation exchange  
3     material, the silica-based material and the proton conducting polymer-based material.

1       15.    The composite electrolyte of claim 1 wherein the composite electrolyte has a proton  
2     conductivity of about 0.05 S/cm or higher

1    16.    The composite electrolyte of claim 1 wherein the silica-based material includes  
2    materials containing one or more of silica, silicate, and silicate having an organic element.

1    17.    The composite electrolyte of claim 1 wherein the silica-based material is either  
2    colloidal silica containing discrete spheres of silica or tetraethylorthosilicate.

1    18.    An electrochemical fuel cell, comprising:

- 2                 (i)      an anode;
- 3                 (ii)     a cathode;
- 4                 (iii)    a fuel supply to the anode;
- 5                 (iv)     an oxidant supply to the cathode; and
- 6                 (v)      a composite electrolyte positioned between the anode and cathode and  
7                 including
  - 8                     (a) an inorganic cation material,
  - 9                     (b) a silica-based binder, and
  - 10                  (c) a polymer-based binder,

11                wherein the inorganic cation exchange material comprises about 0.1 wt% to about 99  
12                wt%, of the composite electrolyte.

1    19.    The electrochemical fuel cell of claim 18 wherein the silica-based material comprises  
2    about 0.1 wt% to about 70 wt%, and the proton conducting polymer-based material  
3    comprises about 0.1 wt% to 99.9 wt% of the composite electrolyte.

1    20.    The electrochemical fuel cell of claim 18 wherein the inorganic cation exchange  
2    material comprises about 0.1 wt% to about 30 wt%, the silica-based material comprises about  
3    0.1 wt% to about 30 wt%, and the proton conducting polymer-based material comprises  
4    about 40 wt% to 99.9 wt% of the composite electrolyte.

1    21.    The electrochemical fuel cell of claim 18 wherein the inorganic cation exchange  
2    material is selected from the group consisting of clay, zeolite, hydrous oxide, and inorganic  
3    salt.

1    22.    The electrochemical fuel cell of claim 21 wherein the clay includes an  
2    aluminosilicate-based exchange material selected from the group consisting of

3 montmorillonite, kaolinite, vermiculite, smectite, hectorite, mica, bentonite, nontronite,  
4 beidellite, volkonskoite, saponite, magadite, kenyaite, zeolite, alumina, and rutile.

1 23. The electrochemical fuel cell of claim 21, wherein the clay is modified to make it  
2 more compatible with organic matrices, a clay modification including exfoliation which helps  
3 to separate platelets of inorganic substance.

1 24. The electrochemical fuel cell of claim 21, wherein the clay includes a modified  
2 montmorillonite consisting of montmorillonite treated with a modifier material selected from  
3 a group consisting of aminododecanoic acid, trimethyl stearate ammonium, octadecylamine,  
4 and methyl dihydroxy hydrogenated tallow ammonium.

1 25. The electrochemical fuel cell of claim 18 wherein the polymer-based material has  
2 linear, branched, or network morphology.

1 26. The electrochemical fuel cell of claim 18 wherein the polymer-based material  
2 includes material selected from the group consisting of acrylonitrile/butadiene/styrene rubber  
3 (ABS), styrene butadiene/acrylate/acetate polymer blends, epoxides, polypropylene,  
4 polycarbonate, polystyrene, polyethylene, polyaryl ethers, and polysulfones.

1 27. The electrochemical fuel cell of claim 18 wherein the inorganic cation exchange  
2 material, the silica-based material and the polymer-based material comprise 90 wt % or more  
3 of the solids content of the composite electrolyte.

1 28. The electrochemical fuel cell of claim 18 wherein the composite electrolyte when  
2 measured in the substantially dried state consists essentially of the inorganic cation exchange  
3 material, the silica-based material and the polymer-based material.

1 29. The electrochemical fuel cell of claim 18 wherein the composite electrolyte has a  
2 proton conductivity of about 0.05 S/cm or higher.

1 30. A method of fabricating a composite electrolyte for use in an electrochemical fuel  
2 cell, comprising:

3                   (i) applying onto a surface of a substrate a viscous liquid composition of (a) an  
4                   inorganic cation exchange material, (b) silica-based material, (c) a polymer-  
5                   based material, and (d) a solvent-dispersant;  
6                   (ii) spreading the viscous liquid composition to form a uniform thickness layer on  
7                   the substrate; and  
8                   (iii) allowing the solvent to evaporate from the viscous liquid composition to yield  
9                   the composite electrolyte,  
10                  wherein the inorganic cation exchange material comprises about 0.1 wt% to  
11                  about 99 wt% of the composite electrolyte.

1       31.       The method of claim 30, wherein the silica-based material comprises about 0.1 wt%  
2       to about 70 wt%, and the polymer-based material comprises about 0.1 wt% to 99.9 wt% of  
3       the composite electrolyte.

1       32.       The method of claim 30 wherein step (ii) includes drawing the viscous liquid  
2       composition through a doctor blade assembly.

1       33.       The method of claim 30 wherein step (iii) includes heating the viscous liquid  
2       composition.

1       34.       The method of claim 30 wherein the inorganic cation exchange material comprises  
2       about 0.1 wt% to about 30 wt%, the silica-based material comprises about 0.1 wt% to about  
3       15 wt%, and the polymer-based material comprises about 40 wt% to 99 wt% of the composite  
4       electrolyte.

1       35.       The method of claim 19 wherein the inorganic cation exchange material is selected  
2       from the group consisting of clay, zeolite, hydrous oxide, inorganic and salt.

1       36.       The method of claim 35 wherein the clay includes an aluminosilicate-based exchange  
2       material selected from the group consisting of montmorillonite, kaolinite, vermiculite,  
3       smectite, hectorite, mica, bentonite, nontronite, beidellite, volkonskoite, saponite, magadite,  
4       kenyaite, zeolite, alumina, and rutile.

1   37.   The method of claim 35, wherein the clay is modified to make it more compatible  
2   with organic matrices, a clay modification including exfoliation which helps to separate  
3   platelets of inorganic substance.

1   38.   The method of claim 35, wherein the clay includes a modified montmorillonite  
2   consisting of montmorillonite treated with a modifier material selected from a group  
3   consisting of aminododecanoic acid, trimethyl stearate ammonium, octadecylamine, and  
4   methyl dihydroxy hydrogenated tallow ammonium.

1   39.   The method of claim 30 wherein the polymer-based material has a linear, branched, or  
2   netted morphology.

1   40.   The method of claim 30 wherein the polymer-based material includes one of  
2   acrylonitrile/butadiene/styrene rubber (ABS), styrene butadiene/acrylate/acetate polymer  
3   blends, epoxides, polypropylene, polycarbonate, polystyrene, polyethylene, polyaryl ethers,  
4   and polysulfones.

1   41.   The method of claim 30 wherein the solvent-dispersant comprises water, N-methyl  
2   pyrrolidinone, dimethyl sulfoxide, dimethyl acidimide, and dimethylformamide.

1   42.   The method of claim 30 wherein the inorganic cation exchange material, the silica-  
2   based material and the polymer-based material comprise 90 wt % or more of the solids  
3   content of the composite electrolyte.

1   43.   The method of claim 30 wherein the composite electrolyte when measured in the  
2   substantially dried state consists essentially of the inorganic cation exchange material, the  
3   silica-based material and the polymer-based material.

1   44.   The method of claim 19 wherein the composite electrolyte has a proton conductivity  
2   of about 0.05 S/cm or higher.

1   45.   A method for producing a composite membrane, comprising:

- 2       (i)     grinding a sulfonated polyether ether ketone (SPEEK) and clay mixture and  
3                   dissolving the mixture in a distilled dimethylformamide (DMF) to form a solution;  
4       (ii)    heating the solution until it thickens and attains a casting consistency;  
5       (iii)   degassing the solution in a vacuum oven;  
6       (iv)    casting the solution into a film on a glass surface using a doctor blade;  
7       (v)     curing the film; and  
8       (vi)    peeling the film from the glass.

1       46.     The method of claim 45, wherein the dissolving in step (i) is performed by stirring  
2                   for about 2 hours using a magnetic stir bar.

1       47.     The method of claim 45, wherein the solution is stirred while heated, and wherein the  
2                   DMF evaporates.

1       48.     The method of claim 45, wherein the film is about 60  $\mu\text{m}$  thick.

1       49.     The method of claim 45, wherein the curing includes,  
2               (a)     annealing the film in a convection oven, and  
3               (b)     maintaining the film in a vacuum for a predetermined time period at a  
4                   predetermined temperature.

1       50.     The method of claim 45, further comprising:  
2                   storing the film in ultra-pure water until it is ready for use.